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Measures for Air Quality

Annual Report—FY 1971

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1972

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[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D.C. 20234.
[2] Part of the Center for Radiation Research.
[3] Located at Boulder, Colorado 80302.

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UNITED STATES DEPARTMENT OF COMMERCE
Maurice H. Stans, Secretary
NATIONAL BUREAU OF STANDARDS • Lewis M. Branscomb, Director

NBS TECHNICAL NOTE 711

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Measures for Air Quality, Annual Report—FY 1971

J. R. McNesby and R. Byerly, Jr.

Institute for Materials Research
National Bureau of Standards
Washington, D.C. 20234

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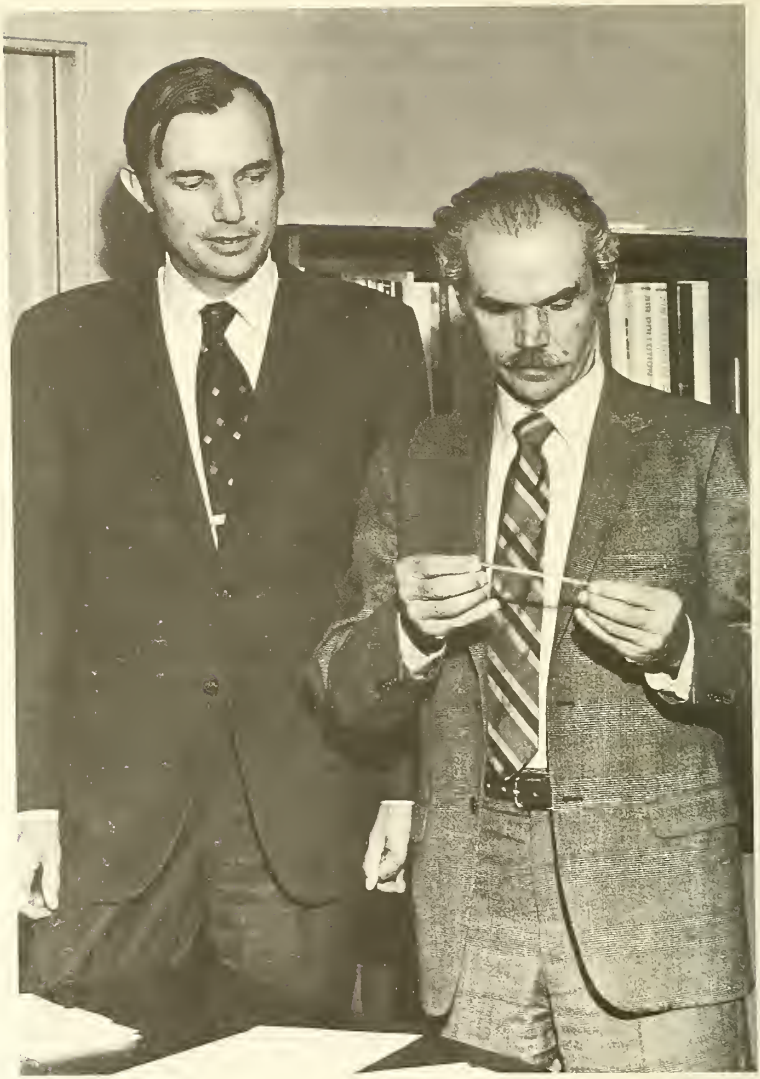


Dr. L. M. Branscomb, Director of NBS, has just presented a sulfur dioxide permeation tube to Dr. John Middleton, Commissioner of the National Air Pollution Control Administration.

TABLE OF CONTENTS

Introduction---------- 1
Executive Summary---------- 6

Major MAQ Projects

Optical Measurement of Particle Size Distributions---------- 8

Determination of the Size Distribution of Airborne Particulate Matter in Real Time by a Light Scattering Method---------- 13

Separations and Identification of Carcinogens Adsorbed on Particles---------- 16

Particulate Reference Material---------- 20

Identification and Structure of Crystalline Components of Particulate Matter in Air Pollution Samples---------- 22

Indoor Air Pollution---------- 24

Electron Energy Loss Spectroscopy of Pollutants-- 26

Molecular Complexes of Gaseous Pollutants-------- 29

Frictional Degradation of Rubber---------- 33

Modulated Infrared Laser Absorption Techniques for Atmospheric Pollutant Measurements------- 37

Atomic Emission Detector---------- 39

The Role of the Lowest Excited Metastable State of SO_2 in the Photochemical Production of Air Pollutants---------- 41

Collection and Evaluation of Physico-Chemical Data for Air Pollutants---------- 46

Air Pollution Chemistry---------- 48

Minor MAQ Projects

NBS Air Sampling Station----------51

Far IR Carbon Monoxide Monitor----------53

Chemical Composition of Polluted Air----------56

Field Emission Spectroscopy----------59

Identification of Free Radicals in Smog Mechanisms----------61

Calibration Standards Via Pyrolysis----------63

Fluorescence Detector for SO_2----------64

Nitric Oxide SRM Development----------65

EPA Projects

Instrumentation Assistance to the National Air Pollution Control Administration----------67

The Sulfur Dioxide Permeation Tube----------68

The Nitrogen Dioxide Permeation Tube----------70

Ozone----------71

Emissions of Rubber from Auto Tires----------72

List of Publications, FY 1971----------73

MEASURES FOR AIR QUALITY

Annual Report
FY 1971

The Measures for Air Quality Program has now completed the first year of its activity. The program, operating formally out of the Institute for Materials Research, is a NBS-wide research effort whose purpose is to advance air pollution measurement science. The MAQ office operates with a staff of three, the manager, his deputy, and one secretary. An important part of the program is to avail the staff of the opportunity to hear lectures by air pollution experts and to be kept abreast of important developments in problem areas of air pollution measurement. To this end, a number of MAQ seminars were held as indicated in Table 1 and a newsletter, the MAQROSCOPE, was produced approximately bimonthly.

It is important that the MAQ effort be responsive to the needs of EPA and of American industry. The MAQ officers, therefore, made a special effort during the past year to increase our contact with EPA people responsible for implementation of the EPA measurement mission and with the industrial sector.

TABLE 1

MAQ Seminars

J. R. McNesby, "Explanation of the MAQ Program and Other Organizational Details." September 16, 1970.

S. N. Milford, "Dispersion of Air Pollutants in Large Urban Areas." September 23, 1970.

W. D. Lee, "Environmental Quality Control Functions of the Bureau of Domestic Commerce." September 30, 1970.

Solomon Zaromb, "Lidar Spectroscopy in the 265-295 nm Wavelength Range." October 14, 1970.

Walter Braun, "Two Recent Optical Techniques Applicable to Detection of Trace Amounts of Air Pollutants." November 23, 1970.

Julian Heicklen, "The Photochemistry of Urban Atmospheres." November 17, 1970.

L. Kreuzer, "Ultrasensitive Infrared Spectroscopy Techniques for Gas Detection." November 2, 1970.

Robert L. Byer, "Optical Methods to Determine the Amount of Gaseous Pollutants in the Atmosphere." December 9, 1970.

James Hodgeson, "Chemiluminescence Applied to Air Pollution Monitoring." February 10, 1971.

Pat McCormick, "The Application of Laser Radar to Measurement of Air Pollution in the Earth's Atmosphere." March 10, 1971.

George Gordon, "Purpose and Operation of the National Industrial Pollution Control Council." May 11, 1971.

The interest of EPA in NBS immediately prior to the MAQ rogram was apparent in their support of the development f calibrated permeation tubes for SO_2 and NO_2 as well as f a calibrated photochemical ozone generator. The elationship between NBS and EPA has become more broadly ased during the past year with the increased emphasis at BS on development of measurement methods.

The MAQ program extended its industrial contact by rranging the placement of an ASTM Industrial Research ssociate in residence at NBS. Dr. Richard Johns, the IRA rom ASTM, is conducting research on permeation tube alibration devices in conjunction with his Project hreshold activity. MAQ officers have established close ontact with the automobile industry through the Air ollution Research Advisory Committee of the auto industry's oordinating Research Council. Additional industrial elationships have been established with a number of ndustrial associations and individual industrial orporations. A large number of letters were sent to air ollution-connected industries inviting them to participate n our program on an industrial research associate basis. nly ASTM has accepted this invitation.

Foreign participation has been solicited through a umber of science attaches at U.S. embassies. Dr. Billon rom France is on board as the FY 72 year begins.

The research effort may be divided roughly into three funding categories, Major Projects in which at least $5K was provided by the MAQ Office, Minor Projects receiving a few hundred to a few thousand dollars in RTS support, and EPA Projects. The progress reports that form the body of this first annual MAQ report are categorized in this way. It is noteworthy that some of those in the Minor Projects category will be (by virtue of the new interest generated by the early results) elevated to the status of Major Projects in FY 1972.

A MAQ Steering Committee consisting of NBS scientists advises the program manager on the content and other facets of the program. The Committee composition is given in Table 2. In FY 72, an Evaluation Panel will serve the program and will hold its first meeting in November.

JAMES R. McNESBY, Manager
Measures for Air Quality

RADFORD BYERLY, Jr.
Deputy Manager

TABLE 2

MAQ Steering Committee

Arnold Bass

Earl Beaty

John Herron

Charles Hunt

Rolf Johannesen

Phillip Klebanoff

Harold Raveché

Louis Santone

John Taylor

Executive Summary

It is characteristic of any research program that some projects are more successful than others and the MAQ program is no exception to this characterization. At the outset, we identified the major measurement problems as SO_2, particulates, nitrogen oxides and ozone with hydrocarbons and CO of second priority. Significant advances have been made in two general areas, new measurement techniques and development of standard reference materials for calibration of monitoring instruments. Among the more definitive advances made during the first year are:

(1) The design and construction of the first apparatus capable of measuring particle size distribution in less than one minute.

(2) The experimental measurements (of fluorescence and quenching, etc.) necessary for the design of the first specific, interference-free, real-time apparatus for measuring sulfur dioxide in the ppm region. Development is continuing on a prototype instrument to extend the measurement range to ambient concentrations. It is noteworthy that this success was achieved in a project classified by us as a "minor MAQ project."

(3) Standard Reference Materials were developed, partly under EPA sponsorship, for monitoring ambient SO_2 and carbon monoxide. In progress are projects whose objectives are to develop SRM's for oxides of nitrogen and ozone.

Some projects, seeded by the MAQ program have stimulated interest in other agencies concerned with air pollution. For example, the National Institute for Occupational Safety and

Health now supports substantial research efforts in two NBS Divisions partly as a result of research stimulated by MAQ and catalyzed by the MAQ office. The Department of Transportation has recognized the application of the MAQ project on evaluation of physico-chemical data for air pollutants to DoT problems in stratospheric pollution by the SST and now supports a major effort in this area in an NBS division.

There are a number of other projects whose prognosis is not entirely obvious at this point in time. Descriptions of these projects as well as those to which reference has already been made, appear in the following pages.

We have taken the position that the most effective route to a compatible, accurate air pollution measurement system is through an integrated program involving methods research, SRM development, and method evaluation including collaborative testing to establish accuracies. This position has been stated and amplified repeatedly to other agencies of the government, the Congress, industrial organizations and at public meetings. We believe that the development of an accurate, compatible measurement system is critical to our nation's effort to implement the Clear Air Act.

OPTICAL MEASUREMENT OF PARTICLE SIZE DISTRIBUTIONS

PROJECT LEADER - D. Jennings and B. Woodward

OBJECTIVE

To demonstrate the feasibility of determining the distribution of sizes of suspended particulates by means of laser light scattering.

APPROACH

The feasibility is to be demonstrated first by a computer simulation of a scattering experiment, then by an actual experiment.

Figure 1 shows schematically an "ideal" experiment in which one detects light scattered at angle θ.

In the simulation the first step (after computer programming, etc.) is to calculate the angular distribution of scattered light intensity which one would expect from a particular distribution of particles. In other words, the Mie theory is used to calculate the angular dependence of the light scattered from one particle. Then a weighted sum is taken over different size particles. The result represents the data one would obtain from an experiment in which a stream of air laden with particles with the assumed sizes is passed through a laser beam and the scattering is measured as a function of angle (see Fig. 2).

In step two of the simulation with this data (which has had some information "averaged out") one uses the Mie theory to

calculate the particle size distribution. Thus the final calculated distribution can be compared to the initial (input) distribution. If the comparison is good, the experiment may be feasible.

The experimental approach will depend on results of the simulation.

PROGRESS

1. The computer programs have been written, assembled, tested and used.

2. Using several representative particle size distributions as input, scattering "data" have been calculated. From the calculated data, various size distributions have been computed. An example is shown in Figure 3. Only spherical particles with a single known index of refraction have been treated. These routines are clearly able to give reasonable solutions for moderately complicated distributions, providing the data accuracy is great enough. If actual experimental data yield results of this quality, such results would represent a striking advance in the particle sizing field.

3. The real experiment has been considered and planning done. Problems are the accuracy needed and the wide dynamic range of scattered light intensity (~3 orders of magnitude, Fig. 2). Basic equipment has been collected and tested. The design of a suitable scattering volume has been considered.

4. Since it is not clear that the experiment can be done to the required accuracy and because the ultimate results (in terms of practical air pollution measurements) are too uncertain, it has been concluded that the project should not be continued.

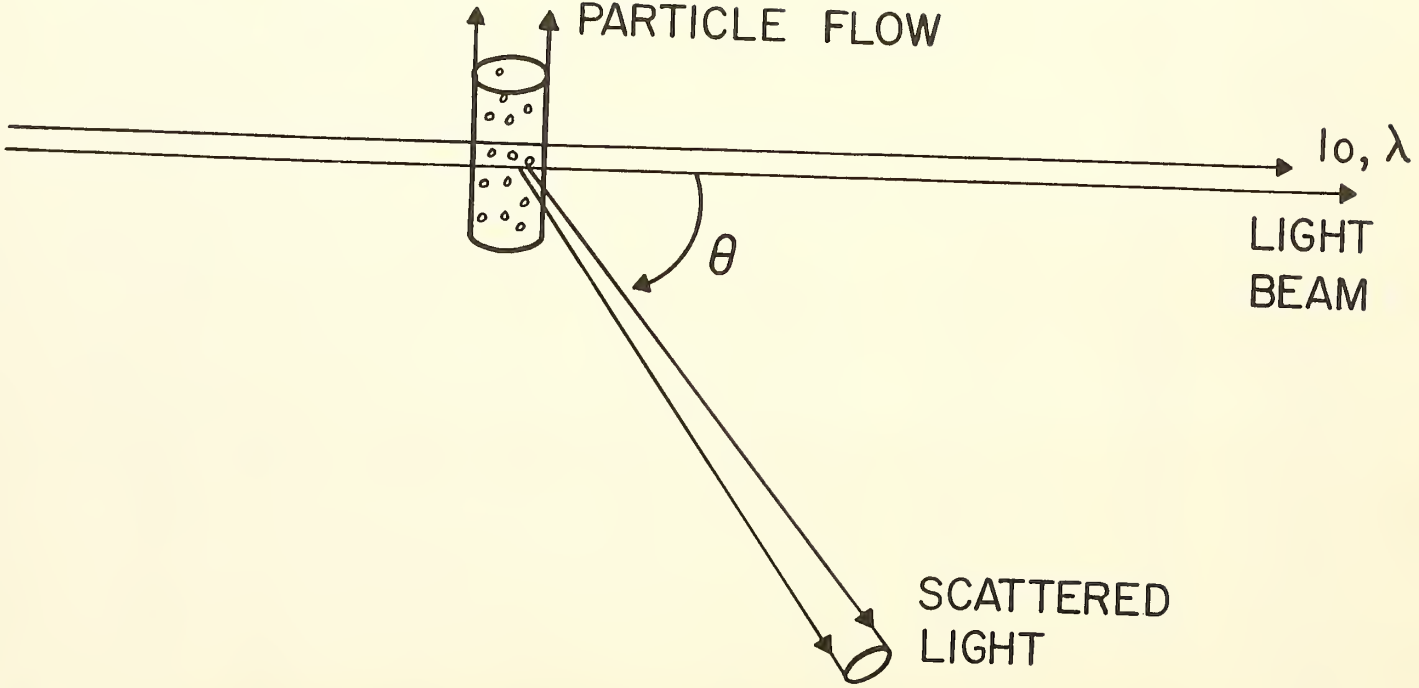


FIGURE 1. "IDEAL EXPERIMENT"

SCATTERED INTENSITY

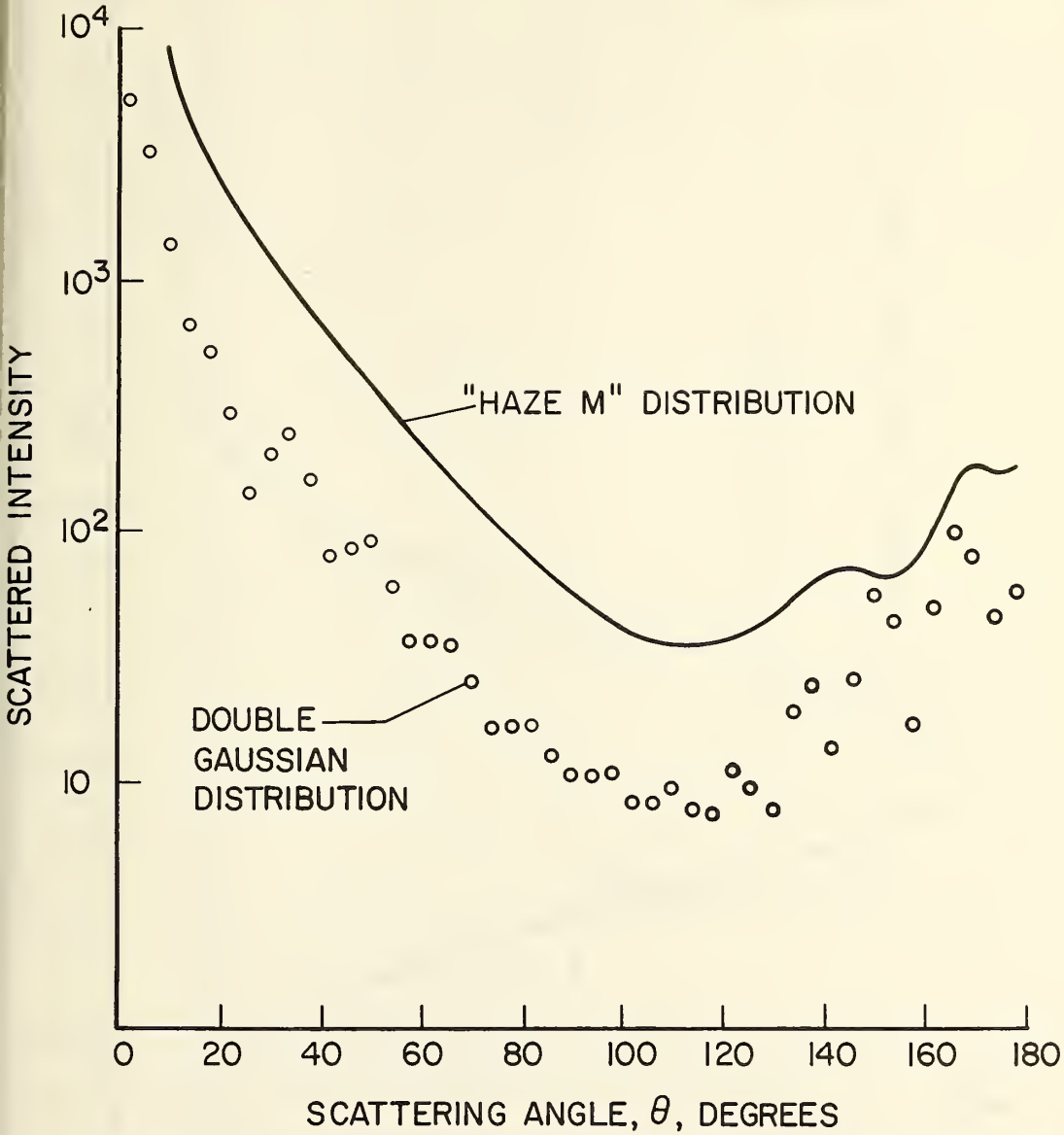


FIG. 2. DIFFERENTIAL SCATTERING--SIMULATED DATA FOR TWO DIFFERENT SIZE DISTRIBUTIONS

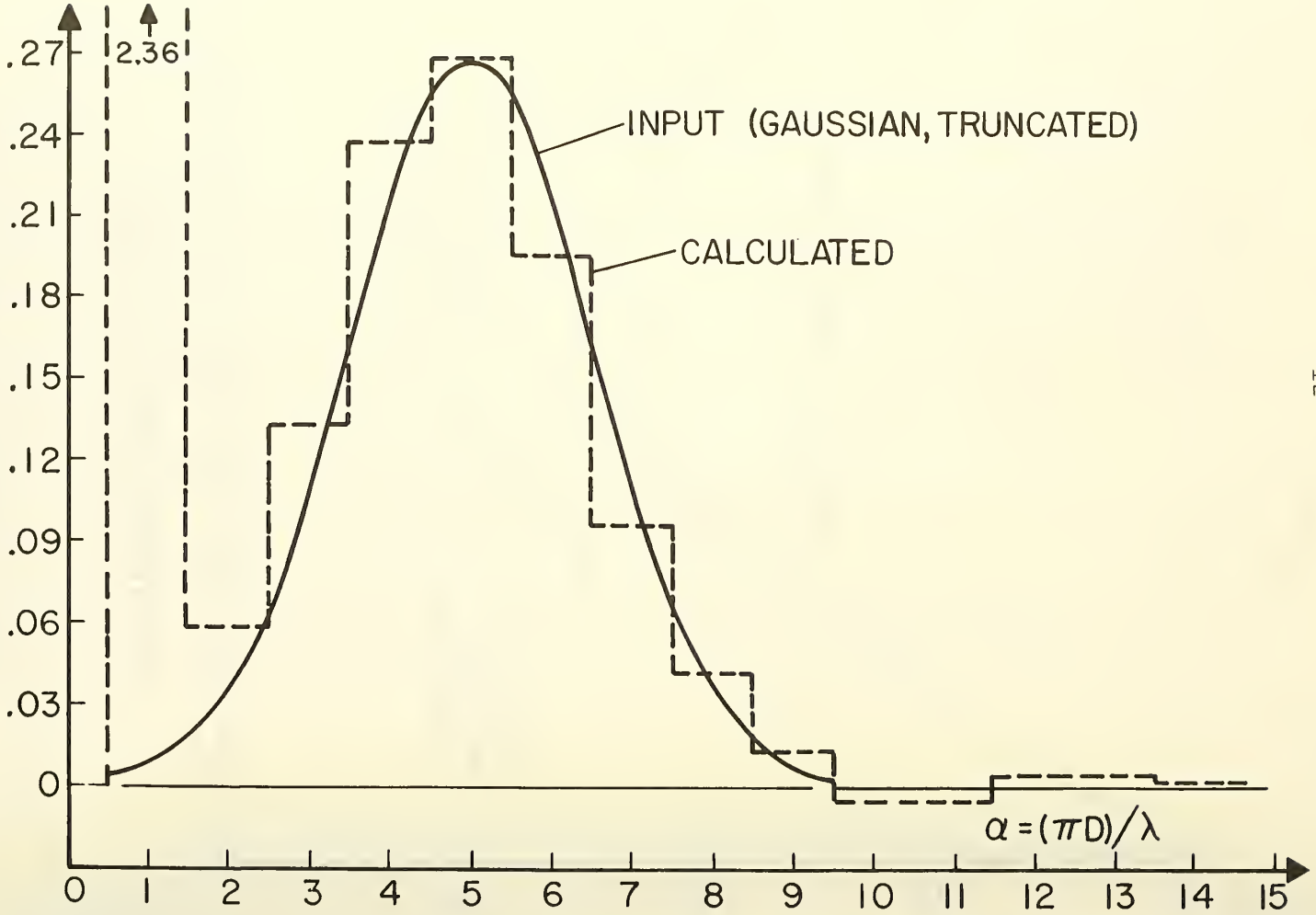


FIG. 3. INPUT AND CALCULATED SIZE DISTRIBUTIONS

DETERMINATION OF THE SIZE DISTRIBUTION OF AIRBORNE PARTICULATE MATTER IN REAL TIME BY A LIGHT SCATTERING METHOD

PROJECT LEADER - C. C. Gravatt

OBJECTIVE

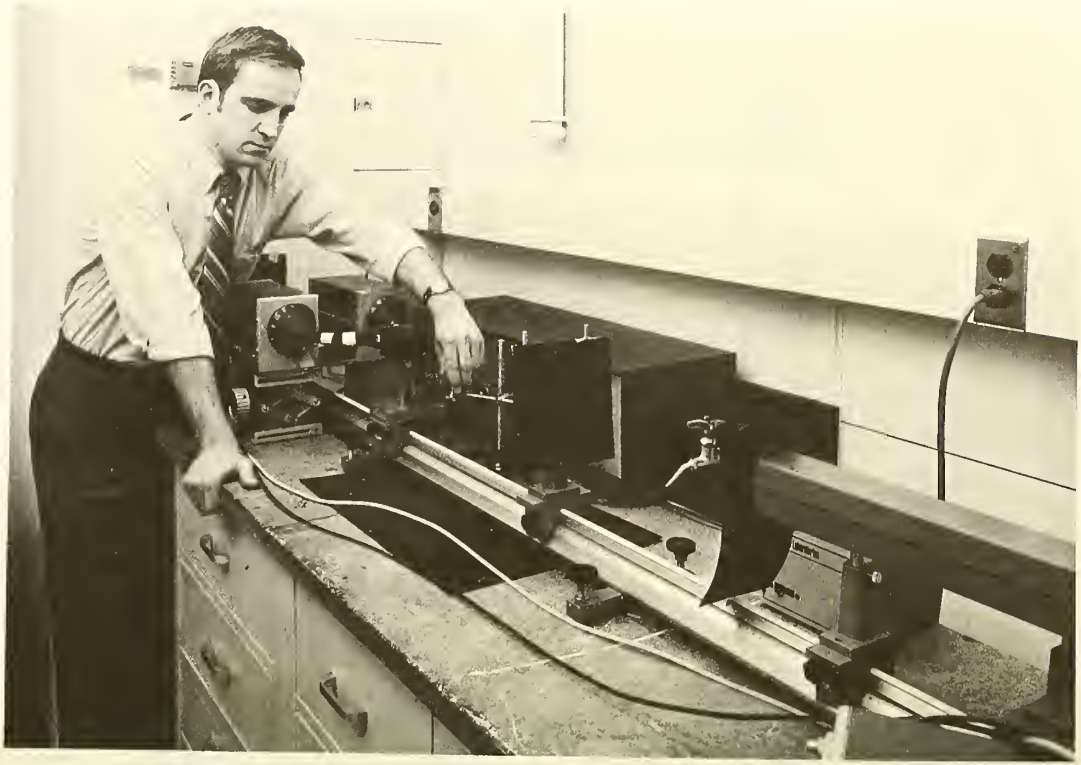
This project will study the determination of the size distribution and chemical composition of particulate matter in air by a light scattering method.

APPROACH

The basic concept involves the simultaneous measurement of the intensity of light scattered by a single particle at two small scattering angles as it is borne by air flowing through a scattering chamber. The ratio of the two scattered intensities is proportional to the radius of gyration of the particle, independent of its index of refraction. Since the particles are measured singly and in real time, simple pulse counting (and known flow rates) give number densities. By employing two wavelengths of light it is also possible to determine the index of refraction of the particle and thereby gain information related to the chemical composition.

PROGRESS

Work performed during FY 71 has dealt with the first objective, the determination of the radius of gyration of the particles. An optical system was designed and built which employs a 3 mw He-Ne laser as source and an annular ring scattered light system which monitors the scattering at 5^{o} and 10^{o}. The



Dr. C. C. Gravatt and his scattering apparatus. The fiber optics which lead the scattered light to the photomultipliers are clearly seen.

use of fiber optics in the scattered light system permits the collection of essentially all of the scattered radiation without a complicated lens arrangement. An analog electronic system has been developed to generate a pulse, proportional to the ratio of the two scattered intensities, which is then counted in a 100-channel multichannel analyzer to provide the real time display. The electronic system is now being modified to improve its sensitivity and response time.

In the immediate future the system will be tested and calibrated using polystyrene sphere samples of known diameter. Then samples will be made up of materials of different index of refraction to study the response of the system to index variations.

SEPARATIONS AND IDENTIFICATION OF CARCINOGENS ADSORBED ON PARTICLES

PROJECT LEADER - David H. Freeman

OTHER PERSONNEL - Walter L. Zielinski, Jr., Rosalie M. Angeles, Delmo P. Enagonio, Edwin C. Kuehner, and Herbert D. Dixon

OBJECTIVE

To develop a method for separation and analysis of certain air pollutant carcinogens. Specific attention is focussed upon polynuclear aromatic hydrocarbons (PAH), such as benzo [a] pyrene (BaP), and the related family of known carcinogenic agents. The method is intended to be simple, give meaningful measurements, be applicable to complex mixtures, and to be adaptable for automatic instrumentation.

APPROACH

Liquid chromatography is the chosen area of study for the PAH carcinogen analysis problem. The experimental methods are used non-destructively at moderate temperatures (10-80°C), they offer high sensitivity, automatability, and high resolution capabilities that equal or exceed those of gas chromatography. Commercial apparatus can be prohibitively costly so that simple apparatus design is of necessary interest.

The present application of interactive gel chromatography, developed recently at NBS, is especially suitable for PAH chromatography and analysis. Specific interactive capabilities

can be built into gel network structures and large quantities of such material can be prepared homogeneously. This is an important base for interlaboratory standardization. The effort to synthesize a suitable gel network is therefore a vital part of the present investigation. The determination of successful interactive gel synthesis lies in the demonstration that the required separations are obtained, that they produce the needed isolation of specific carcinogenic components in real samples as well as synthetic mixtures, and that they are amenable to appropriate standards and calibration procedures.

PROGRESS

A. Apparatus. A do-it-yourself approach to apparatus design for liquid chromatography was developed. It provides versatility and control that are lacking in costly commercial LC systems. The apparatus is easily assembled, or modified. Apparatus fabrication guidelines were developed on the basis of reasoning by analogy to simple DC electrical resistive circuits. Two reports on this are being prepared for publication.

B. Theory. The basis for the theoretical development resides in the extensive scientific literature on organic molecular interactions that occur in liquid media. The ability of conjugate organic solutes to undergo weak association, or interaction, to form a complex, is well known. In general, acid-base conjugates have the ability to donate or receive a binding electron pair or active proton. Such interactions lead to the formation of an acceptor:donor complex.

An interactive gel is prepared so that it will interact with conjugate solute species to form a complex. The strength of a given complex is related to the solute affinity for the permanently affixed structural groups in the gel. Differences in affinity provide the basis for the separation of different molecular species present in a mixture. A theoretical treatment of the solute:gel interactive processes, including the role of competitive solvent interactions, has been prepared for publication.

C. Stationary Phase Synthesis and Testing. Non-interactive gels were initially studied in order to test their ability to separate carcinogenic compounds on the basis of molecular size. On this basis we can now specify and we have samples of network superstructures in which relatively large PAH molecules, such as BaP, have full permeability.

A proton acceptor gel, crosslinked polyvinylpyridine, was found to interact strongly with proton donor solutes. The protons in an aromatic system were found to be too weakly acidic for successful PAH separation by this gel.

The delocalized (π) electron density should be especially significant for the achievement of chemical separation of PAH compounds. The π electrons in BaP type molecules can form a complex with a π electron acceptor such as silver, or electron donor such as iodine (I_2); this is already known. We described the occurrence of the latter process chromatographically, and the finding was recently published.

Silver:BaP complexation has become our present major target for gel synthesis. Initially, we bound $AgNO_3$ onto a polyvinylpyridine gel. This gave negligible ^{3}BaP interaction, however. More recently we prepared a porous cation exchanger in the silver ion form and the material shows good

compatibility with organic solvent systems. The material gave a pronounced separation factor for weak π electron donors (benzene, anthracene) from the stronger base, BaP. The chromatography at this point is crude but very promising. The synthetic development and testing of refined gel network structures is continuing.

PARTICULATE REFERENCE MATERIAL

PROJECT LEADER - John K. Taylor

OTHER PERSONNEL - Staff of Division 310 (ca. 15 people)

OBJECTIVE

To develop techniques and procedures for the certification of an atmospheric particulate reference material as a means for evaluation of chemical analysis of particulates.

APPROACH

The reliability of chemical analysis of particulate matter is uncertain, largely because no means of evaluation are available. Analytical work must be done on expendable samples and there is no means to intercompare either results by the same laboratory or by different laboratories. It is the intention to obtain a large quantity of representative atmospheric particulate matter, and to exhaustively analyze it, using a multi-competence approach. This material would be made available as either an SRM or a research reference material. Recipients would be encouraged to report the results of their findings, which would be included in revised reports on the material.

PROGRESS

We have been unable to obtain a large source of particulate matter. A small sample (100 g) of material collected in New York City was made available to us by EPA.

This material has been used to establish the feasibility of the concept and to develop methodology for use when a large sample is available. The measurements included: Morphology; general descriptive data; elemental analysis by emission spectroscopy, atomic absorbtion spectroscopy, polarography, spectrophotometry and neutron activation analysis; anion determinations by wet chemical methods; group determinations of organic constituents. All studies showed that it is feasible to produce a particulate reference material. A detailed report of the measurements is in preparation. A design of a bag-house type collector has been developed, that could be constructed for about $40K. It would permit collection of about 10 lbs. of material per month.

IDENTIFICATION AND STRUCTURE OF CRYSTALLINE COMPONENTS OF PARTICULATE MATTER IN AIR POLLUTION SAMPLES

PROJECT LEADER - Howard E. Swanson

OBJECTIVE

Determination of the crystalline compounds in airborne particulate matter and the distribution of these compounds in a city environment.

APPROACH

Using X-ray diffraction analysis we will study dustfall samples from a large industrial city. Identification of compounds rather than just the elements involved in this material should be useful in establishing sources of particulate matter.

PROGRESS

Three sets of one month accumulation dustfall samples have been obtained from eight sampling stations in Baltimore, Maryland, for the months of December, February, and March. Most of these samples were of sufficient quantity to fill a regular size x-ray sample holder and give good workable diffraction patterns.

With one exception, the bulk of these samples were quite similar The major portions showed the same compounds found in fly ash produced in large coal burning plants. (Fly ash from the Black Dog Power Plant in Minneapolis, Minnesota, sent to Dr. Byerly by Stanford Research Inst. was used in this comparison).

The products were mainly: SiO_2 (quartz), Fe_3O_4 (magnetite) with smaller amounts of Fe_2O_3 (hematite) and $CaCO_3$ (calcite), plus some unburned coal and amorphous silicates.

Material from one sampling station showed approximately 75% αAl_2O_3 (corrundum) for one collection period but only small amounts during the previous and following periods.

Other materials noted in small amounts were: C (graphite), $CaSO_4 \cdot 2H_2O$ (gypsum), $CaMg(CO_3)_2$ (dolomite), and questionable indications of $Cu_{0.6}Zn_{0.4}O$, Zn, and a complex calcium silicate.

No arrangements have been made as yet to obtain samples of airborne products from specific industries, but it is evident from the diffraction patterns we have that such products could be traced to some of the dustfall stations.

Two NBS spectrographic analyses for this Baltimore area served as a check in comparing elements with the compounds found by diffraction analysis.

A separate investigation of asbestos minerals for the Encyclopedia of the Solid State has helped to build technical background that could be useful in any future involvement with asbestos as a hazardous material.

INDOOR AIR POLLUTION

PROJECT LEADER - Charles M. Hunt
ASSOCIATE INVESTIGATOR - Barry C. Cadoff

OBJECTIVE

To determine the type and composition of pollutants of indoor air, to develop methods for measuring them under laboratory and field conditions, to determine the source of indoor pollutants, and outdoor pollutant levels.

APPROACH

It is planned to develop a mathematical model of indoor-outdoor pollution relationships, initiate tracer studies of air movements in buildings, conduct a survey of indoor pollutants and study control and abatement aspects of the indoor pollution problem.

PROGRESS

A simple model of an air conditioned building with forced air ventilation has been developed by which both the steady state ratio of indoor to outdoor pollutant, as well as the rate at which steady state is approached can be computed. More important, the model provides a basis for analyzing the effects of changing parameters such as the relative amounts of recirculated air and fresh air or the efficiency of the air cleaning system on indoor/outdoor pollutant relationships.

A tracer technique using sulfur hexafluoride (SF_6) and an electron capture detector is being evaluated as a possible tool for measuring flow rates in buildings and elsewhere. Tests

in a duct with known concentrations of SF_6 indicate that the electron capture detector performs as a convenient detector in the 5-50 ppb range. Toxicological information on SF_6 is being gathered.

Paper tape and high volume sampler measurements indicate that indoor dust levels in the Building Research Building were usually lower than outdoor levels. Emission spectra of the collected dust indicated that lead was a consistent trace element in both indoor and outdoor dust. Infrared spectra of indoor and outdoor dust were different, probably due to more silicates in outdoor dust. Ammonium sulfate, which probably originates in the atmosphere, has been identified as a constituent of indoor air at Gaithersburg. This is discussed in a short prepared discussion submitted to the American Society of Heating, Refrigerating, and Air Conditioning Engineers in connection with a symposium on indoor air pollution.

Simple measurements of particles generated in a room by smoking, and operation of a vacuum cleaner or an electric fan have been made with a light scattering particle counter. Household aerosol sprays such as "air fresheners" and certain cleaning aids and deodorants are being investigated as particle generators.

One of the needs at the present time is to develop measurement capability for trace gases and vapors in indoor air. This, as well as much of the material in the foregoing summary, is discussed in NBS Report 10591 "Indoor Air Pollution Status Report."

ELECTRON ENERGY LOSS SPECTROSCOPY OF POLLUTANTS

PROJECT LEADER - Chris E. Kuyatt

OTHER PERSONNEL - Stanley R. Mielczarek, Physicist
Miss Jane E. Doyle, Technician

OBJECTIVE

To develop the high resolution electron spectrometer as a gas analysis tool. This task includes the determination of the limits of sensitivity of the electron spectrometer for typical pollutants in air and for typical components of automobile exhaust.

The goal is to develop analysis techniques and computer programs for the electron spectrometer which will achieve sensitivities in the part per million range.

APPROACH

The approach is to measure electron energy loss spectra for pure gases at known pressures and under controlled conditions of the electron spectrometer. To reduce the effect of instrumental variations, spectra will be calibrated with a reference gas using either static or dynamic mixing or both. Binary mixtures of known composition will then be prepared and their energy loss spectra recorded. The spectra will be analyzed either graphically or via digital computer and sensitivity and accuracy determined. Multi-component mixtures will then be investigated, for example NO in air and NO in a mixture typical of automobile exhaust.

PROGRESS

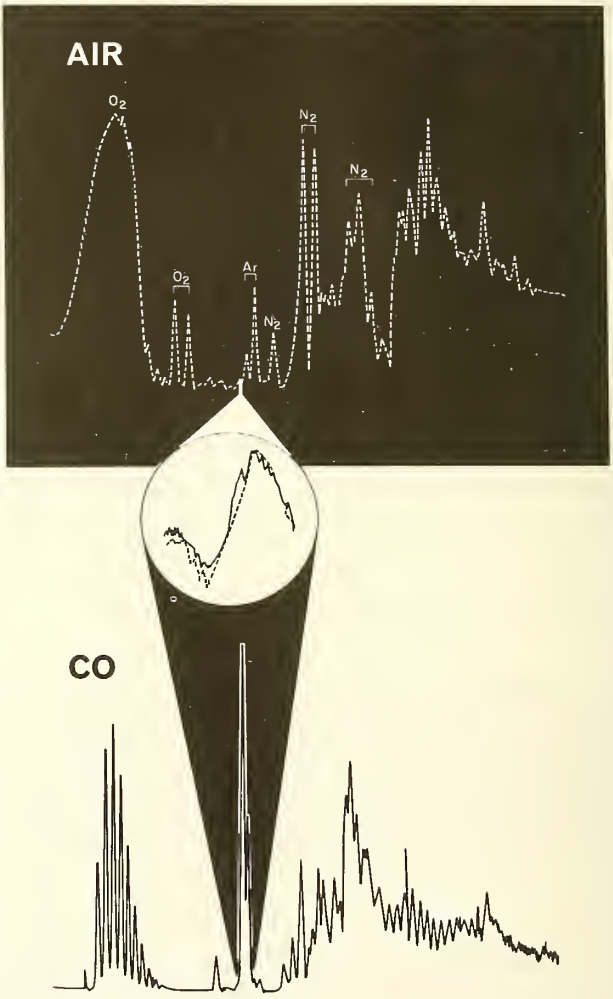
The necessary pure gases and liquids have been obtained. Gaseous samples are used as supplied from compressed gas tanks. Liquid samples are specially prepared to free them from dissolved gases by several cycles of freezing, pumping, and melting.

Spectra have been obtained for O_2, N_2, CO_2, Ar, He, H_2O, NO_2, and SO_2 as well as for several molecules of special interest to the parallel AF project: methane, benzene, acetone, n-hexane, ethyl alcohol, trichloro-ethylene, and N_2O. The spectra are in the form of both X-Y recordings and punched paper tape obtained via a small on-line computer.

Calculations of gas flow in the inlet system of the electron spectrometer showed that the concentration of each component in a gas mixture is enhanced by the square root of its molecular weight. This result will be checked experimentally using the gas mixing system described below.

To obtain an absolute calibration for each pure gas spectrum, helium will be added at a known concentration by either static or dynamic mixing. A special gas handling system for both mixing methods has been designed, constructed, and installed. Testing of the calibration and mixing procedures has begun.

For all but the simplest gas mixtures, analysis of a composite spectrum into its constituents is best done by computer fitting. Spectra recorded on punched paper tape using a small computer-operated data system will be entered into a time-sharing computer system via an acoustic coupler from the teletype in our laboratory. We are currently reformatting the paper tape into a form suitable for the time-sharing computer and writing a spectrum analysis program based on linear least squares programs.



Top: Electron energy loss spectrum of air containing a small amount of CO. Bottom: Pure CO spectrum. Insert: The air spectrum enlarged to show the measured and fitted CO line.

MOLECULAR COMPLEXES OF GASEOUS POLLUTANTS

PROJECT LEADER - J. J. Ritter
OTHER PERSONNEL - R. C. Paule

OBJECTIVE

As originally conceived, this project sought to prepare and characterize molecular complexes of pollutant gases suitable for use as analytical standard reference materials. While the original concept is still of interest, we have chosen (a) to broaden the scope of the investigation to include a variety of approaches to the problem of NO standards, and (b) to abandon, for the present, research on complexes of gases other than NO.

APPROACH

(1) The suitability of mercury-encapsulated gas bubbles as certifiable standards will be experimentally investigated for the specific case of SO_2. (2) The concept of a permeation device for NO based on a chemical system functioning as a NO reservoir under an equilibrium NO pressure of 1 atmosphere or more will be investigated. (3) A third approach to NO standards envisages the use of a selective reducing agent in combination with a source of NO_2. Given a reliable source of NO_2 which is capable of delivering that gas into a carrier gas stream at a known rate, a reducing module placed downstream of the NO_2 source could convert the latter to a NO source. The combination could be certified as a unit, or, if the reduction stoichiometry were sufficiently reliable, the combination could operate in either the "NO mode" or the "NO_2 mode."

PROGRESS

1. Encapsulated Gas Bubbles--A paper describing the techniques for preparation and use of these microstandards has been submitted to Environmental Science and Technology. The microbubble standards are considered to be particularly promising for preparation of gas mixtures containing relatively high levels of SO_2 for which present permeation tubes are not satisfactory. Preliminary experiments indicate that the microbubble concept is also applicable to NO.

2. NO Permeation Tube--The permeation of NO through a polytetrafluoroethylene (PTFE) tube has been examined. In separate experiments, NO gas at about atmospheric pressure and NO over a solution of $CuCl_2$ in ethanol were used as gas sources. It was concluded that acceptable permeation rates can be obtained under these conditions. It is of interest that no permeation of solvent was noted in the solution experiment, suggesting that solution phases may be satisfactory sources of NO if other requirements can be met.

The lack of data on the reversibility of NO uptake by metal ions has inhibited selection of a suitable reservoir complex from among the compounds already in the literature. A literature report [Fraser and Dasent, JACS 82, 348 (1960)] suggested that a simple electrolytic cell using non-aqueous solutions of $CuCl_2$ might be applicable as a source of NO for a permeation device. Consequently, electrolysis of the deep purple solutions of $CuCl_2$ with nitric oxide in ethanol and acetonitrile was investigated. In contrast to the results of the earlier workers, however, we found no production of gas at the cathode in these systems, apparently because degassed solutions were used in our experiments. The electrochemical approach was therefore abandoned.

We believe that the combination of the molecular complex concept with the permeation tube principle offers an attractive approach to NO standards. It is apparent, however, that exploratory synthesis work will have to be carried out to find the suitable NO source material for use in such a device.

3. Reducer Module NO Generator--Development of the "reducer module" requires selection of a suitable reaction system capable of converting NO_2 to NO at a definite stoichiometry and at low levels of incident NO_2. The module itself could either be a catalytic convertor or contain a consumable reagent. For practical reasons, a solid catalyst or reagent system is preferable.

A simple reaction system has been constructed for evaluation of candidate materials for the reducer module. A commercial NO_2 permeation tube has been used as the source of the gas. Reactions of NO_2 have been studied in three systems up to the present:

(a) Reaction with hydrogen over platinized alumina catalyst. This system was selected on the basis of patent literature reporting stepwise reduction of NO_2. The system has been shown to be extremely sensitive to operating parameters. Under various conditions, NO, NH_3, and N_2O are obtained. The uptake of hydrogen by the catalyst system strongly influences the course of the reaction, making precise control difficult. This approach has consequently been abandoned in favor of a non-catalytic system.

(b) Reaction of NO_2 with MnO. This system is typical of many potential candidate systems employing low-valency transition metal compounds. It proved to be effective for reduction of NO_2 to N_2O.

(c) Reaction of NO_2 with Cu. Reduction of NO_2 to NO was obtained. Not surprisingly, considerable loss of $(NO)_x$ was observed, presumably a result of compound formation.

It has been learned from Stevens at EPA that passing NO_2 over hot gold wool affects its reduction quantitatively.

A fourth, somewhat specialized concept is under consideration in connection with MAQ interest in stratospheric monitoring of atmospheric pollutants. As described in an informal summary previously provided to MAQ, it appears feasible to adapt the principle of the King Piezoelectric Sorption Hygrometer to the detection of gases other than water by providing selective adsorption sites on the surface of the piezoelectric crystal. Existing coupling agent technology suggests possible routes to surface preparation. A demonstration experiment in our laboratory on an available model system has shown reversible NO uptake by copper-doped aluminosilicate structures.

FRICTIONAL DEGRADATION OF RUBBER

PROJECT LEADER - James E. Fearn
ADVISORY - Joseph M. Antonucci
Roland E. Florin

OBJECTIVE

The objective of this work is to determine the products of frictional degradation of rubber and from these to deduce the mechanism and basic nature of this degradation. These observations should illuminate the problems associated with the permanence of rubber as a material and as a source of pollution.

APPROACH

The present approach to the study of the degradation of rubber involves the abrasion of rubber specimens of known composition under clearly defined and controlled conditions. These conditions include placing the rubber specimens under different loads and moving them over the abrasive surfaces at various velocities. The atmospheres under which the frictional studies take place may be varied, .e.g., air, nitrogen, helium, vacuum etc. Abrasive surfaces may include aluminum, or indeed any other metallic surface, as well as asphalt, concrete, glass, etc. Products from these experiments are collected and analyzed.

PROGRESS

Pursuing the objective mentioned above and the approach, the following apparatus (see attached photograph) was constructed. A glass cylinder with diametrically opposed side arms was attached to an aluminum base plate through a

flange joint equipped with an O ring and a screw clamp which provided a gas-tight seal. This base plate is so equipped that the abrasive surface may be securely attached to it. Through the top of the glass cylinder a steel shaft carrying the rubber sample is introduced by employing a ferro-fluid feedthrough seal coupled with a steel bellows. This arrangement permits translational motion of the shaft while maintaining again a hermetic seal. The shaft is connected to the chuck of a drill press with a capacity for maintaining both a constant load on the rubber sample and a constant angular velocity.

The side arms on either side of the glass cylinder permit the withdrawing of samples in any desired fashion, the admission of any desired atmosphere, or the attachment of any required evacuating system.

The apparatus described above has been tested and the customary irregularities have been corrected. Most of these irregularities dealt with maintaining a gas-tight system during abrading operations. Preliminary experiments included the abrasion of an ASTM polyisoprene prototype in a helium atmosphere under from 1 to 5 lb loads for 30 minutes or less. The time limit was necessary because of the tendency of the rubber sample to adhere to the abrading surface, in this case an aluminum disc. Very little evidence of light volatile material was indicated from a GLC examination of this system. Placing greater weight on the rubber sample produced shredding of the sample and some smearing in the abrasion area. This abraded material showed solubility in benzene in contrast to the total insolubility of the original sample. The benzene solution of the abraded sample was filtered through a millipore filter and a sample was subjected to GLC, yielding indication of a low concentration of a

substance presumed to be isoprene. It was observed that aluminum oxide often interfered with analysis. Tackiness of some of the abraded samples suggests high temperatures during the actual process. Efforts are underway to modify the apparatus so that a thermocouple may be introduced to determine the maximum temperature during the experiment.

Abrasion Apparatus

MODULATED INFRARED LASER ABSORPTION TECHNIQUES FOR ATMOSPHERIC POLLUTANT MEASUREMENTS

PROJECT LEADER - Melvin Linzer

OBJECTIVE

Theoretical development of frequency-modulated laser absorption techniques for remote and point sampling of air pollutants.

APPROACH

The basic technical areas explored were frequency modulation of infrared lasers, absolute intensity measurements, and sensitive detection schemes. Both line-of-sight propagation for path-average measurements and lidar methods for pollutant profile mapping were examined.

PROGRESS

Design criteria for a frequency-modulated laser absorption instrument have been developed and the basis for future experimentation is now available. The proposed device would have the capability of detecting and quantitatively measuring extremely small concentrations of pollutants, even in the presence of large atmospheric and optical system losses. Both very short and very long path measurements as well as long-range lidar measurements would be possible.

The MAQ Office has decided not to fund this effort into an experimental stage. The theoretical analysis of the frequency-modulated laser techniques will be prepared for publication. An experiment embodying principles not specifically developed for this study, but nonetheless pertinent to its objective, has been scheduled in collaboration with Bell Laboratories. A

Raman spin-flip laser source will be used in conjunction with an opto-acoustic detector to measure infrared absorption in dimethylmercury.

ATOMIC EMISSION DETECTOR

PROJECT LEADER - Walter Braun, A. M. Bass
Technician: A. Ledford

OBJECTIVE

Develop an absolute detector for measurement of gaseous air pollutants based upon emission from excited atoms produced in a discharge.

APPROACH

An air sample injected into a helium stream separated into its constituents by gas chromatography. The effluent gas stream is subjected to a microwave discharge and the emission from the excited atoms so formed is measured.

PROGRESS

It was found that pollutant molecules containing sulfur gave a signal at the sulfur emission line proportional to the concentration expressed as sulfur atoms. The detector was, therefore, found to be absolute. Carbon-containing molecules were found to behave in a similar fashion. The original plan was to assist the Analytical Chemistry Division in assaying standard CO samples (1 to 100 ppm in air). The samples were originally made by weight and the question of whether these samples deteriorated with time was an important consideration. When the original proposal was made, the analytical chemists were not set up to perform CO assays. However, at about the time this project was begun, the situation had changed, and the analytical people were now

quantitatively converting CO into methane and analyzing their samples via flame ionization detection. Several of their samples were checked and very good agreement (within several percent) was found.

A second project was undertaken: The analysis of small amounts of NO in nitrogen (1 to 100 ppm) by measuring the atomic nitrogen emission. Since nitrogen is present to the extent of 10^6 times that of NO, we required adequate chromatographic separation between NO and N_2. Various column packing materials were employed without success.

We consider these efforts important for the following reasons:

(a) There is at present no absolute chromatographic detector commercially available. For air pollution monitoring, an absolute detector is needed.

(b) Improvements have been made in the original design and in its overall capability. As a result of these efforts, a better detection system will be possible.

THE ROLE OF THE LOWEST EXCITED METASTABLE STATE OF SO_2 IN THE PHOTOCHEMICAL PRODUCTION OF AIR POLLUTANTS

PROJECT LEADER - Richard Keller
OTHER PERSONNEL - Christer Hellner, Allan Laufer

OBJECTIVE

(a) To produce and characterize the spectral properties of metastable species of SO_2 formed by the absorption of light by SO_2.

(b) To study the reactions of these metastable species with common atmospheric constituents.

(c) To study the photochemical properties of these metastable states.

(d) To use the results of (a)-(c) to assess the role of metastable species of SO_2 in air pollution.

APPROACH

(a) Use a high intensity (18 Kj) flash photolysis apparatus to produce large concentrations of metastable species.

(b) Use conventional flash spectrographic techniques to measure the visible and ultraviolet absorption spectra of the metastable SO_2 species. Extinction coefficients will be determined.

(c) Study quenching by common atmospheric constituents. An attempt will be made to determine and characterize chemical products of these quenching reactions.

(d) Use a tunable laser to produce selectively metastable SO_2 species with well-characterized energies. Repeat step (c) with these well characterized species. Produce species with laser and by irradiation with standard photochemical sources in presence of common atmospheric species, study the photochemistry of the metastable species. Determine the wavelength dependence of the reactions and attempt to identify products formed.

PROGRESS

Steps (a)-(c) under Approach have received most attention. Our results are summarized by:

(a) The flash photolysis of SO_2 results in the temporary, complete disappearance of the characteristic spectrum of ground state SO_2 and the appearance of a new broad absorption. This new species is formed by photons of wavelength greater than 300 nm.

(b) The intensity of this absorption decays by a 1st order process and the absorption of ground state SO_2 reappears with the same time constant. There is no significant photochemical decomposition of the SO_2.

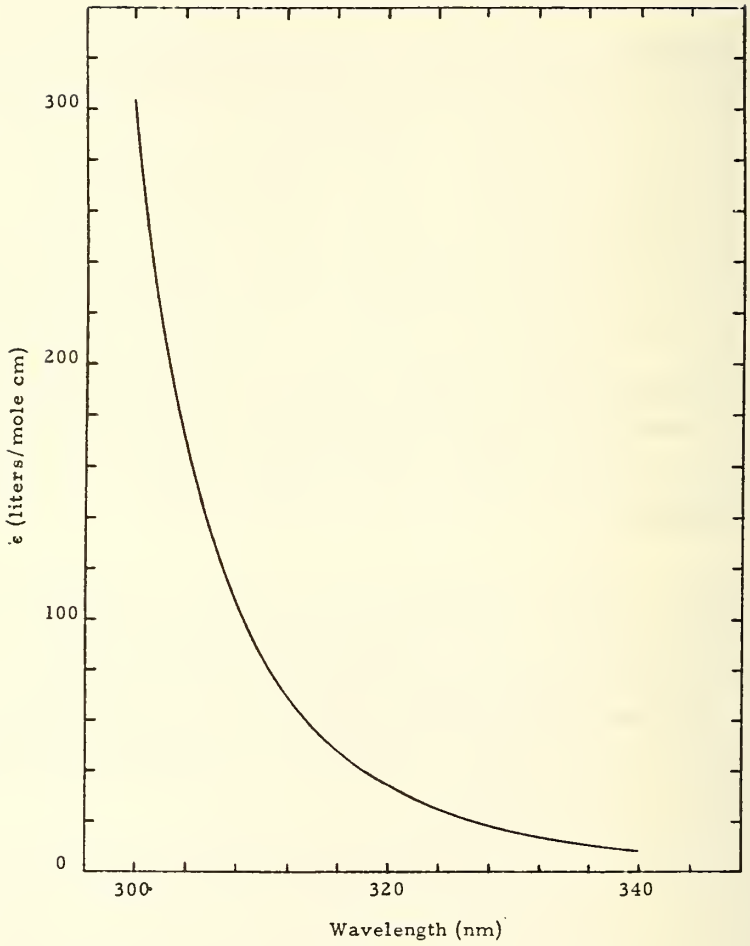
(c) The wavelength dependence and the extinction coefficients of the metastable species have been characterized in the region from 300 to 360 nm (see Fig. 1). The spectral range from 360 to 800 nm was investigated and no absorptions were observed. Work is in progress to investigate the spectral range from 200 to 300 nm.

(d) The observed lifetimes of the metastable species in the presence of SO_2, CO_2, Ar, Xe, He, O_2, and NO were determined. The results of some of these studies are shown in Figure 2. No photochemical decomposition of SO_2 was observed in any of these experiments.

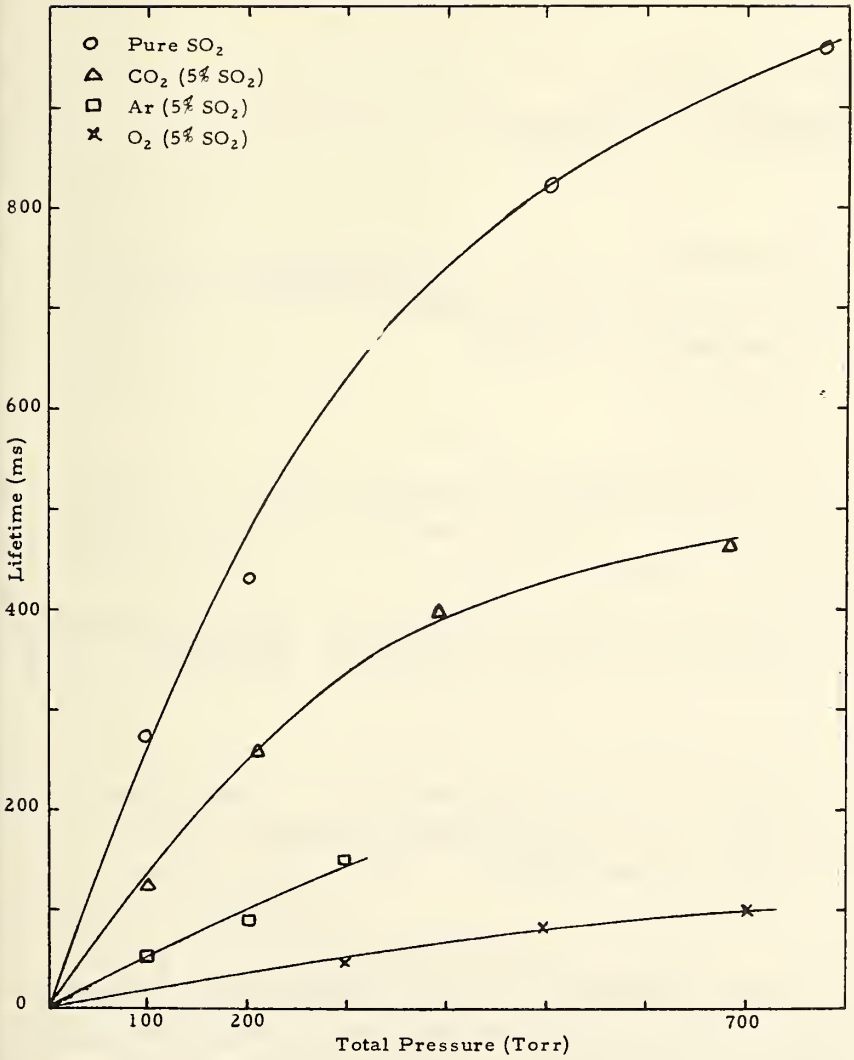
Unfortunately, while we have much information about the properties of the metastable species, we are unable to specify its structure at this time. From Figure 2, it is seen that in some cases the lifetime of this species approaches one second at high pressures. Note also that in all cases the lifetime increases as the pressure of the added gas increases. We feel that the long lifetime and the pressure dependence of the lifetime indicate that the metastable species is not an excited electronic state of SO_2. Other possibilities are isomeric species of SO_2 or complexes formed between excited SO_2 molecules or between an excited SO_2 molecule and a ground state molecule.

In summary, flash irradiation in the UV of SO_2 results in a metastable species. This metastable species has a long lifetime, does not react with common atmospheric species, decays to give ground state SO_2, and is not an excited electronic state of SO_2. Work is in progress to attempt to identify this species.

Absorption Spectrum of Metastable Species
Formed From Excited SO_2



Lifetime of Excited SO_2 as a Function of Total Pressure in Presence of Foreign Gases



COLLECTION AND EVALUATION OF PHYSICO-CHEMICAL DATA FOR AIR POLLUTANTS

PROJECT LEADER - D. Garvin

OTHER PERSONNEL - R. Hampson

OBJECTIVE

This project, has as its goal the publication of a series of data sheets (or a handbook) on the physical and chemical properties of atmospheric pollutants.

APPROACH

The initial set of pollutants to be studied was O, O_3, NO_2, CO, CO_2, SO_2, C_2H_4 and "PAN" (peroxyacetylnitrate). We have found it desirable to expand this list to include OH, NO, N_2O, N_2O_5 and excited molecular oxygen, since their reactions with the other species are often of potential importance.

PROGRESS

Preliminary Data Sheets have been prepared for O_3 and PAN. Data sheets for O and NO_2 are essentially complete. Work on the others is at various stages.

Most of the effort has gone into an assessment of the photochemical and reaction rate data. We have tabulated the likely reactions of the species of interest with each other and with trace constituents of the polluted atmosphere and have collected the relevant papers.

During this phase it has become apparent that we must revise our procedures in order to improve productivity. To this end, single data sheets on a process or reaction are now being prepared.

Physical property data has been collected for us by others. Each of these represents a major effort. The work is merely summarized here.

Thermochemical Properties	E. Domalski, J. Minor
Transport Properties (an extensive report, emphasizing theory)	H. Hanley
Microwave Spectrum	W. Kirchhoff
High Resolution I.R. Spectra	S. Abramowitz

In addition, we have collected material from NSRDS monographs and manuscripts.

Recent developments - During the past six months a controversy has developed about the possible effect of high flying aircraft on the ozone layer of the atmosphere. Study of the manuscripts showed that this is principally a photochemical and chemical kinetics problem. It was decided that the Physical Chemistry Division should review the relevant data for preparation of a set of data sheets. These are to provide basic input data for atmospheric modelling.

Accordingly, a task force has been assembled to complete this job during the summer of 1971. During July approximately 10 data sheets have been prepared. Our goal is about 50. Interestingly enough, many of the reactions are also pertinent to tropospheric pollution. The evaluations made by this task force will be used in the basic handbook.

AIR POLLUTION CHEMISTRY

PROJECT LEADER - J. T. Herron
OTHER PERSONNEL - R. E. Huie

OBJECTIVE

The objective of this project is the kinetic characterization of the elementary reactions which may play an important role in air pollution chemistry. Specifically, this includes the reactions of atomic oxygen, singlet molecular oxygen, ozone and hydroxyl radicals with primary organic pollutants, and with the oxides of nitrogen and sulfur.

APPROACH

The approach used is a combination of laboratory studies with data compilation and evaluation.

The laboratory programs center around the NBS chemical kinetics mass spectrometer, used for the study of atomic oxygen and singlet molecular oxygen chemistry, and the resonance fluorescence apparati at NBS and at the University of Maryland used for the study of atomic oxygen reactions.

In the case of the atomic oxygen reactions, the laboratory program is designed to complement the data evaluation program by establishing absolute rate constants for key reactions to be used in converting the existing large body of relative rate measurements into absolute rate constants, and to provide data on important reactions where none exists or where the existing data is unreliable.

PROGRESS

The principal accomplishments in FY 1971 have been in the measurement and evaluation of atomic oxygen rate constants, and in the study of the reactions of singlet molecular oxygen.

Rate constants have been measured over a wide range of total pressure and temperature for the reaction of atomic oxygen with ethylene. This is the key reaction in the evaluation of the kinetic data on the reactions of atomic oxygen with organic compounds.

Rate measurements have also been completed for the reactions of atomic oxygen with the cycloalkanes, and 1-butene. Nearing completion is work on the haloalkenes, the higher olefins, O_2 and NO_2. The latter two being of particular interest in stratospheric chemistry, are being studied at temperatures down to 220 K.

The data compilation and evaluation on atomic oxygen--organic compounds is underway and should be complete by about September (to appear in Progress in Reaction Kinetics and as part of the NSRDS series).

A compilation of rate constants at 300 K covering 104 reactions has been prepared for use in the NBS Air Pollution Handbook.

An important objective of the work on singlet molecular oxygen was the evaluation of chemical titration methods for the measurement of singlet molecular oxygen concentrations. We have compared 2,5 dimethylfuran, tetramethylethylene, and N,N-dimethylisobutenylamine as titrants and found that only 2,5-dimethylfuran was suitable. To confirm the validity of

the titration, we have used an argon resonance lamp in conjunction with a pair of parallel plate electrodes to compare the relative photoionization cross sections of C_2H_2, C_2H_4, NO, and $O_2(^1\Delta_g)$ (as measured by titration). The values found by us are in excellent agreement with those found by other workers, and lend strong support to the titration technique.

In addition to evaluating titration methods, we have measured rate constants for $O_2(^1\Delta_g)$ reactions over a range of pressure (0.5 to 8 torr). We find no evidence for a pressure effect and conclude that the large body of relative rate data obtained from solution studies as well as from low pressure gas phase work is transferable to real atmospheric situations. From this in turn we conclude that singlet molecular oxygen plays an insignificant role in the oxidation of organic molecules in the atmosphere.

NBS AIR SAMPLING STATION

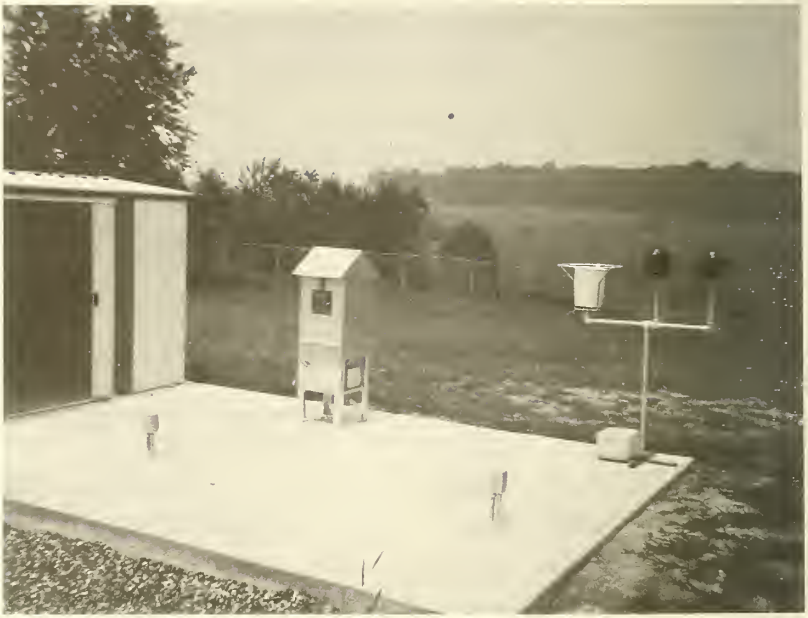
PROJECT LEADER - John K. Taylor
OTHER PERSONNEL - Rolf A. Paulson

OBJECTIVE

To establish an air monitoring station on the NBS site. This station will then be used not only to provide local air quality data, but will give firsthand information on the problems involved in such measurements.

APPROACH AND PROGRESS

The location for the station was selected after numerous discussions with NBS officials. A concrete platform 10' x 20' was constructed with four power outlets. An aluminum shelter building 7' x 10' was erected. Monitoring equipment was purchased. The station is now in operation for measurement of total particulates, dustfall, and sulfation. Other measurements will be made as equipment becomes available. The station will permit familiarization of NBS staff with available instrumentation under field conditions and it is the intention to do this.



NBS Air Monitoring Station

FAR IR CARBON MONOXIDE MONITOR

PROJECT LEADER - H. A. Gebbie

OBJECTIVE

Design and construct an apparatus to measure CO concentrations to be expected in automobile exhausts.

APPROACH

Measurement of far IR absorption in the pure rotational spectrum of CO using the properties of a two-beam interferogram will be attempted. Multiple path traversal through the sample will be achieved by means of a non-resonant spherical cavity.

PROGRESS

A device has been constructed as shown in Figure 1, which includes a stepped mirror interferometer to increase selectivity. The steps are designed to match specific parameters of the CO molecule. Distinguishing features of the design are:

1. Use of the non-resonant spherical cavity to enhance the absorption.

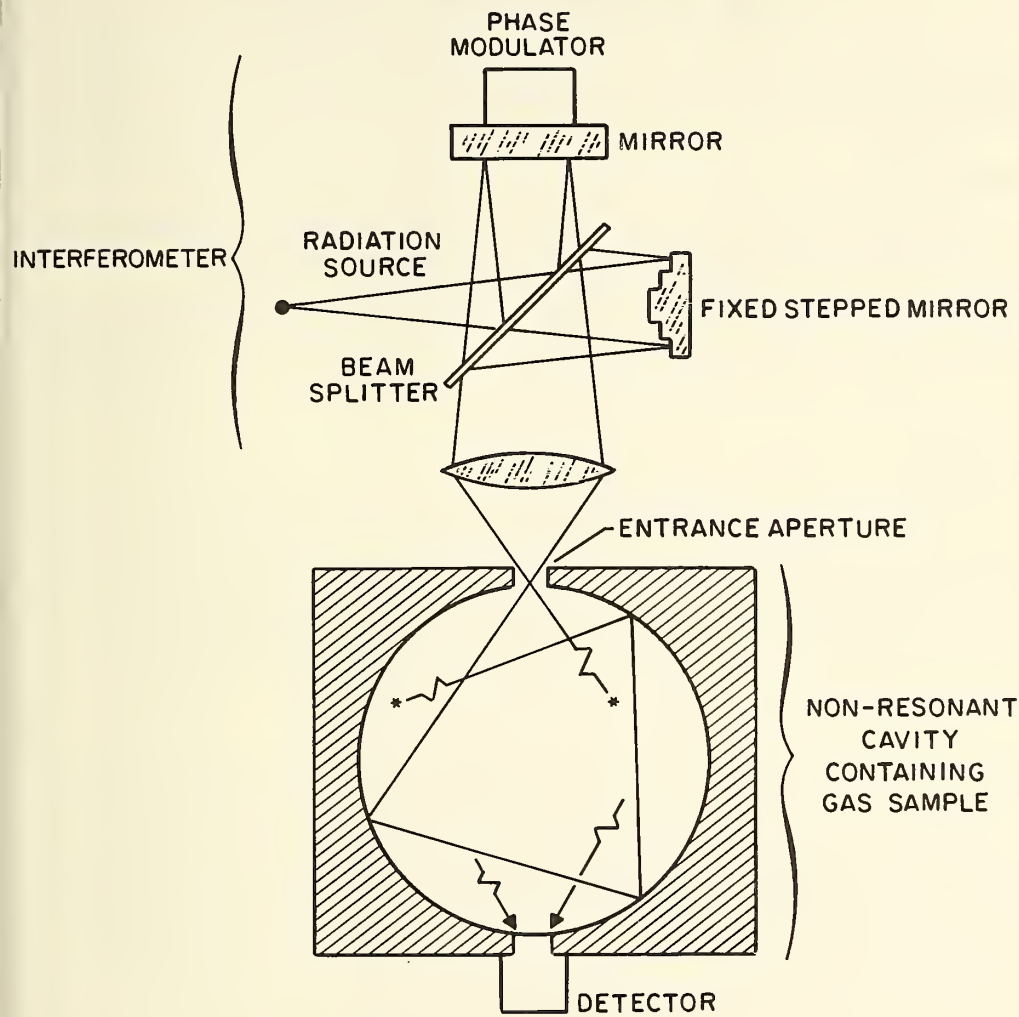
2. The stepped mirror is fixed in position and is not scanned.

3. The output of the (thermal) detector measures directly the amount of CO in the sample cell.

4. The only moving part is the vibrating mirror of the phase modulator.

The only serious interference is H_2O which is readily removed from the sample by conventional techniques. Carbon dioxide does not interfere since it has no far IR absorption.
A number of typical vehicle exhausts has been analyzed including idling modes. The limit of detection in the present prototype appears to be approximately 0.3 percent CO.

GAS ANALYSER USING A NON-RESONANT CAVITY ABSORPTION CELL AND A SELECTIVE INTERFEROMETER



PRINCIPAL FUNCTIONS

1. A long absorption path is achieved by the radiation making many passes through the gas because the metal cavity wall has high specular reflectivity.
2. The steps on the mirror are designed to match specific molecular parameters of the gas being analysed.
3. The output of the detector is then a direct measure of the amount of gas in the cavity.

FIGURE 1.

CHEMICAL COMPOSITION OF POLLUTED AIR

PROJECT LEADER - Harold W. Woolley

OBJECTIVE

The project objective is to estimate magnitudes of effects on equilibrium constants and equilibrium compositions of N_2 + O_2 mixtures due to interactions between molecules with particular regard to reactions occurring in automobile power plants. The influence of reaction rates is also considered

APPROACH

A computer program written earlier for high temperature reactions was adapted to the examination of equilibrium properties of N_2 and O_2 perturbed by the presence of CO_2. Values of thermodynamic functions from JANAF tables are read in for each constituent for 20 temperatures ranging from 100 K to 6000 K.

Estimates for effects of interactions on the equilibrium constants and the equilibrium compositions were based on sets of pair second virials, B, and third virial values, C, and their derivatives for major constituents as read in as a short table for several temperatures. This is based on an equation of state in the form

$$PV/RT = \exp(s_1/V + s_2/V^2)$$

where $s_1 = B$ and $s_2 = C - B^2/2$.

PROGRESS

Various modifications of calculation procedures for the approach to chemical equilibrium were examined, depending in part on the particular path for the chemical reactions presumed to be of greatest influence in the process. Calculations have been made for effects on nitric oxide concentrations at equilibrium as a result of varying such conditions as temperature and density and the concentration of carbon dioxide. Several cases such as for the following sets of reactions have been considered:

$$O_2 = 2\,O$$
$$N_2 = 2\,N$$
$$O + N = NO$$

$$O_2 = 2\,O$$
$$N_2 + O = N + NO$$
$$O_2 + NO = O + NO_2$$
$$N + NO_2 = 2\,NO$$

$$O_2 = 2\,O$$
$$N_2 + O = N_2O$$
$$O + N_2O = 2\,NO$$

$$CO_2 = CO + O$$
$$N_2 + O = N_2O$$
$$O + N_2O = 2\,NO$$

It was found that the introduction of CO_2 into the system has no great effect on the equilibrium concentration of NO at any conditions of temperature and pressure specified.

FIELD EMISSION SPECTROSOPY

PROJECT LEADER - Ralph Klein

OBJECTIVE

To study the behavior of NO adsorbed on ruthenium and to use this study to assess the feasibility of using ruthenium as a catalyst for the conversion of NO to the elements.

APPROACH

The method used is that of field emission microscopy in which a field emission tip of ruthenium is centered in a molecular beam of NO. The ruthenium tip temperature is maintained at $4.2^{\circ}K$ during the condensation. Temperature control is such that the ruthenium surface may be heated in an approximately square wave mode to any desired temperature up to the melting point of ruthenium ($2700^{\circ}K$).

PROGRESS

The first observation was that it was impossible to achieve complete coverage of NO on the tip. In the normal procedure the axis of the emitter is perpendicular to the axis of the molecular beam. The emitter tip, "sees" the beam only on its upper half surface. The initial condensation is by way of chemisorption. Completion of the monolayer is followed by physical adsorption. Heating of the tip to a relatively low temperature ($50-60^{\circ}K$) results (with gases observed) in the migration of the physi-sorbed layer to the under side of the tip where it is immediately trapped and chemisorbed. In this way, a tip covered with a monolayer of the gas is prepared.

However, NO proved to be unusual in that, even after long deposition, no migration of the NO to the unexposed portion was observed after heating. Several explanations may be advanced. One, that NO does not condense on a monolayer surface, is very unlikely. Two, the NO is bound so weakly in the second layer that it desorbs before migration. Three, the NO is so strongly bound, even as a physisorbed layer, that much higher temperatures are required for migration of the physisorbed layer, so high that it desorbs before it migrates. Four, disappearance of NO is by way of diffusion into the lattice, also very unlikely. Explanation two is currently favored.

Heating of the tip half covered with NO to still higher temperatures (about 300^{o}K) causes decomposition. The oxygen pattern can then be observed. It is quite clear that NO decomposes very easily on a ruthenium surface. Further studies on this system are in progress.

IDENTIFICATION OF FREE RADICALS IN SMOG MECHANISMS

PROJECT LEADER- Dolphus E. Milligan
OTHER PERSONNEL - Marilyn Jacox

OBJECTIVE

Such species as CH_3O and HO_2 are believed to be important in smog forming mechanisms. Characterization of their spectra in the ultraviolet would enable studies to be made of the kinetics of these species. The objective of this work is to find the ultraviolet spectra of such species.

APPROACH

An attempt will be made to form CH_3O by the vacuum-ultraviolet photolysis of methanol and of its deuterium-substituted counterparts isolated in solid argon and in solid nitrogen at $14^{\circ}K$. The vacuum-ultraviolet photolysis of Ar: O_2:HCl and Ar:O_2:H_2O will be done to produce HO_2 in a matrix.

PROGRESS

Photolysis sources used for these experiments have included the 1470-A xenon resonance line, the 1067-A argon resonance line, and the 1216-A hydrogen line. The highest relative yield of the CH_3O product is obtained using 1470-A radiation. Since there is a well-defined absorption due to this species in the spectral region characteristic of O-H stretching absorptions, it is believed that the structural formula is H_2C-OH. Upon exposure of the sample to mercury-arc radiation of wavelength shorter than 2800-A, photodecomposition of this species occurs, indicating the presence of a continuum absorption in the 2500-2800-A spectral region.

Photolysis of $Ar_2:O_2:HCl$ and $Ar:O_2:H_2O$ samples of mole ratio 200:1:1 have led to the stabilization of considerably higher concentrations of HO_2 than have previously been observed in matrix-isolation experiments. O_3 and H_2O_2 are also produced in significant concentration, and, in the HCl experiments, Cl-O-O and HOCl. Despite these higher concentrations of HO_2, studies of the 1800-9800-A spectral region have not yielded any absorptions which may be assigned to this species, nor does any decrease in the HO_2 absorption result even on prolonged irradiation of the sample by the full light of a medium-pressure mercury arc. A detailed normal coordinate analysis of the vibrational spectrum of HO_2 has been performed on the Univac 1108 computer, and agreement with all of the observed isotopic frequencies is excellent, assuming a valence angle of $105^\circ \pm 5^\circ$.

A manuscript has been prepared and submitted for publication in which detailed infrared spectroscopic studies of the interaction between low-energy electrons and alkali metal atoms and various nitrogen oxides are reported. Most significant to air-pollution studies is the discovery that O^- produced by the interaction of electrons with N_2O persists for a sufficient time in an argon matrix to permit diffusion from the site of its production and reaction with N_2O or with NO to produce detectable concentrations of $N_2O_2^-$ and of NO_2^-, respectively.

CALIBRATION STANDARDS VIA PYROLYSIS

PROJECT LEADER - Wing Tsang

OBJECTIVE

The generation of known concentrations of important pollutants in air.

APPROACH

Specified air pollutants of known concentrations will be synthesized through the pyrolysis of larger and more stable molecules. The pollutant molecule is one of the fragments into which the pollutant decomposes and the other is an easily measured hydrocarbon.

PROGRESS

Demonstrated in a qualitative fashion that this approach will work for formaldehyde, acetaldehyde, sulfur dioxide (butadiene sulfone) and butadiene (cyclohexene). Tests have been limited by the insensitivity of detection devices. New equipment has been ordered. Some calculations have been made with regard to the design parameters for a 1 ppm formaldehyde generator at a flow rate of 50 cc/min and lifetime of 6 months.

FLUORESCENCE DETECTOR FOR SO_2

PROJECT LEADER - H. Okabe

OBJECTIVE

Study the fluorescence stimulated by radiation in the 200- 230 nm wavelength region of spectrum to determine the feasibility of this method for measurement of ambient SO_2.

APPROACH

The feasibility of the fluorescence measurement method requires a knowledge of the absorption coefficient, fluorescence intensity, radiative lifetime and quenching efficiencies by O_2 and N_2. These factors will be studied.

PROGRESS

A lifetime of the excited SO_2 obtained from absorption coefficient measurements was found to be 9×10^{-9} sec. Fluorescence intensity was measured as a function of wavelength and pressure of air in order to determine quenching efficiencies. It was found that in ambient air fluorescence is still measureable and that SO_2 may be measured at ambient concentrations. The result suggests it would be worthwhile to construct a prototype device for measurement of ambient SO_2 and this work is underway.

NITRIC OXIDE SRM DEVELOPMENT

PROJECT LEADER - Ernest E. Hughes
OTHER PERSONNEL - William D. Kinard; Rolf A. Paulson

OBJECTIVE

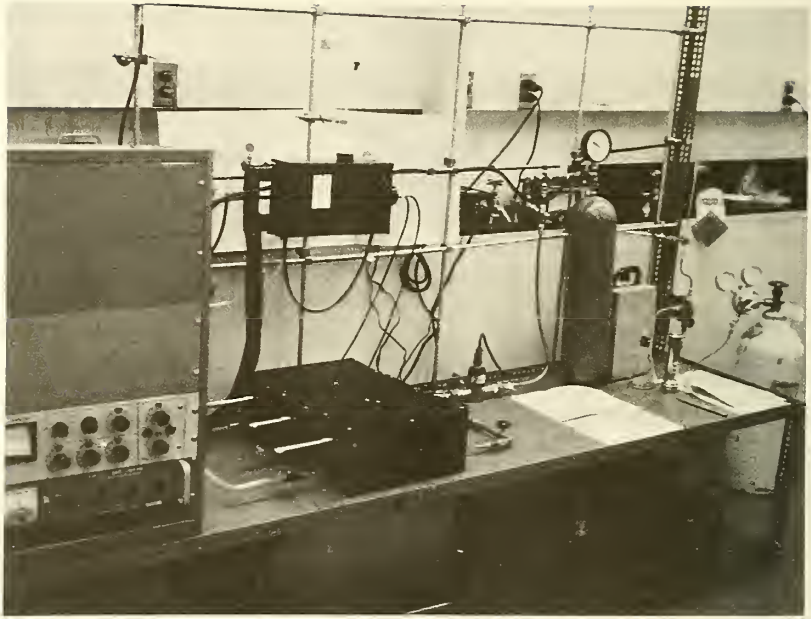
Determine the stability of NO in nitrogen and propane in air for their eventual use as Standard Reference Materials for source testing.

APPROACH

Chemiluminescent reactions provide sensitive and selective methods for nitric oxide analysis. The referee methods for automotive nitric oxide and ambient photochemical oxidant include such techniques. Chemiluminescence apparatus will be constructed and its analytical reliability evaluated for NO measurement. Procedures will be developed for certification analysis of SRMs, including especially the assessment of stabilities of NO-N_2 mixtures in cylinders.

PROGRESS

Components were obtained from which a chemiluminescent system was assembled. The operation of the system has been checked out, using the ozone-ethylene reaction. A procedure is under development for the intercomparison of ozone generators, using the chemiluminescent method. Apparatus for utilization of the ozone-nitric oxide reaction for determination of the latter is being completed, and will be evaluated in the near future. Studies of the stability of NO-nitrogen mixtures in steel cylinders are in progress.



Apparatus for Analysis of Air Pollutants
by Chemiluminescent Techniques

INSTRUMENTATION ASSISTANCE TO THE NATIONAL AIR POLLUTION CONTROL ADMINISTRATION

PROJECT LEADER - G. A. Dines

OTHER PERSONNEL - R. M. McCabe
M. L. Greenough

OBJECTIVE

Process data taken on magnetic tape at the 6 Continuous Air Monitoring Project (CAMP) stations of EPA. Summaries output on paper, detailed output on microfilm.

APPROACH

Develop software to process the data tapes. This involves analysis of the many tape and operator errors at the monitoring stations, and the development of operator procedures and software to either prevent or recover from the errors.

PROGRESS

The software is virtually complete. About 40 reels of data tape have been run so far and the remaining 40 in the backlog will be processed within the next two weeks. At that point, product will be on a current basis.

THE SULFUR DIOXIDE PERMEATION TUBE

PROJECT LEADER - John Taylor and E. Hughes

OBJECTIVE

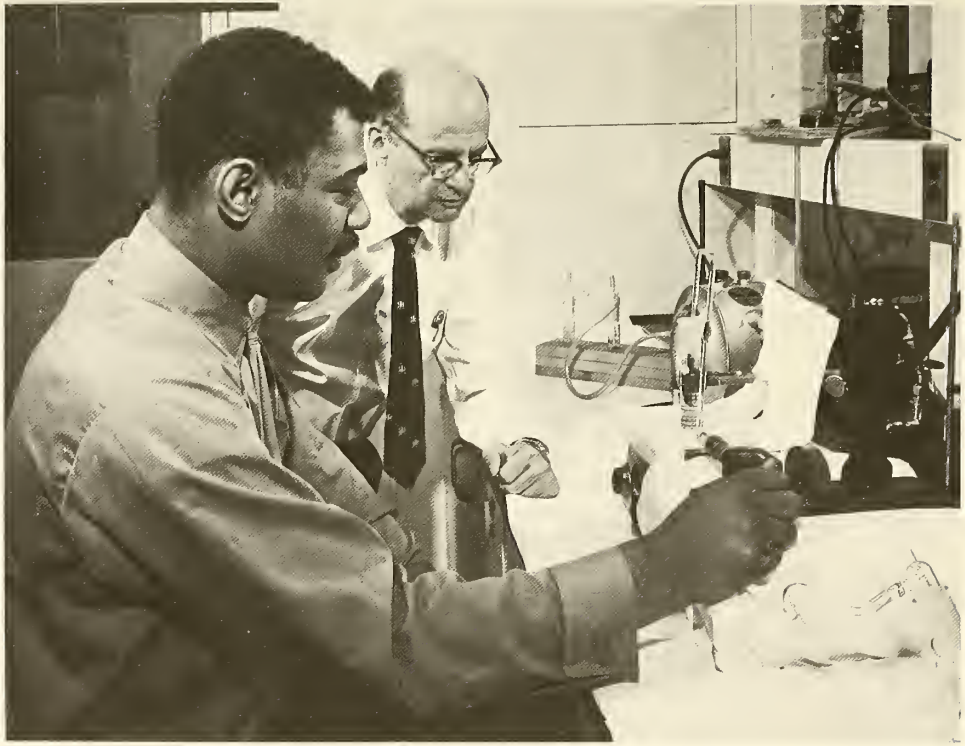
To demonstrate the certifiability of sulfur dioxide permeation tubes as SRMs.

APPROACH

Study the behavior of the permeation tubes over long periods of time under conditions which might be encountered during calibration and use. The tube is made of teflon, in which is contained liquid sulfur dioxide, and has the physical dimensions roughly of a pencil. The effect of accumulations of grease on the tube's exterior, exposure to water,effect of purity of SO_2, were to be investigated along with flow rate and temperature dependence.

PROGRESS

The effect on permeation rate of wall thickness and uniformity was determined. The time taken to reach a constant permeation rate after removal from storage at -20 to -30°C was measured and found to vary from 24-48 hours. Equilibration is achieved reliably only when at least 24 hours is allowed following a temperature change. The effects of these parameters mentioned in the "approach" paragraph were evaluated experimentally. The tubes are useful subject to stringent temperature and flow rate control. Most of the above work was done before the establishment of MAQ and was funded entirely by EPA. On December 1, 1970, Serial No. 1, SO_2 permeation tube was presented by Dr. Branscomb to the Administrator, National Air Pollution Control Administration, Dr. John Middleton (see frontispiece). For details, see NBS Tech. Note 545.



Dr. John Taylor and William Kinard measuring ozone by the neutral buffered KI method.

THE NITROGEN DIOXIDE PERMEATION TUBE

PROJECT LEADER - John Taylor and E. Hughes

OBJECTIVE

To examine the suitability of NO_2 permeation tubes as SRMs.

APPROACH

It is essential for a field calibration permeation tube that its permeation rate be independent of time. Preliminary experiments with NO_2 permeation tubes showed this not to be the case, the rates decreasing monotonically over the life of the tubes. The research program aimed to discover the reason for this behavior and to introduce appropriate measures to ensure a constant rate. Effects of humidity and temperature were to be studied systematically.

PROGRESS

Twenty permeation tubes purchased commercially all showed rates of weight loss decreasing with time over the life of the tube. Further, the rates are inconveniently high for ambient air applications. Reduced rates were obtained by altering the physical dimensions and finally by means of a new design, the microbottle. This consists of an impermeable glass tube capped with a teflon disc through which the NO_2 permeates. It was found that moist air depresses the rate and produces a blistering of the tube. Water, in the form of fuming nitric acid, was found in the tubes that had been exhausted. The introduction of P_2O_5 into the microbottle reduces the rate of the drop in permeation rate by an order of magnitude. Research is continuing on this system. This project is funded entirely by the EPA.

OZONE

PROJECT LEADER - John Taylor, T. Mears

OBJECTIVE

To define conditions under which an ultraviolet light source may be incorporated into a device usable as an SRM for ozone measurement and to fabricate prototype devices.

APPROACH

An ultraviolet light source with output at 184.9 nm is combined with a quartz tube through which air flows at a measured rate. By exposing controllable fractions of the air to the light, varying concentrations of ozone are produced in the air stream. The absolute standard for measurement of the amount of ozone produced is the neutral buffered KI method.

PROGRESS

A number of devices have been fabricated and research is in progresss to relate such parameters as flow rate and time to measured ozone generation rates. This project is funded entirely by EPA.

EMISSIONS OF RUBBER FROM AUTO TIRES

PROJECT LEADER - R. L. Raybold

OBJECTIVE

To determine the fate of material worn from automobile tires.

APPROACH

Since we desire to measure the products of normal wear of tires and since obtaining "normal wear" and capturing the products tend to be mutually exclusive goals, some compromises had to be made. It was decided to run full scale tires, at reasonable speeds and loads inside a closed room so that the products are trapped. Provision is made to measure suspended particulates and volatiles, and to collect particles that fall out.

PROGRESS

Facilities for running tires at up to 35 miles per hour and loads of 1000 pounds around a 14-foot diameter paved track are available at Amoco Research, Whiting, Indiana. A contract was negotiated and let to run the tests. The contractor has begun preparing for the tests which will be run several days in early FY 72. Preliminary analysis of samples of particulate matter collected at the NBS tire testing facility have showed no polynuclear aromatic hydrocarbons. They have also indicated that the material worn from tires in the NBS tests (which are not wear tests) appears to be a degraded material, i.e., not bits of "virgin" rubber. Preparations for the particulate collection during the Amoco tests have been made.

APPENDIX

LIST OF PUBLICATIONS, FY 1971

Herron, J. T. and Huie, R. E., "Mass Spectrometric Studies of the Reactions of Singlet Oxygen in the Gas Phase," Annals of the New York Academy of Sciences 171, 229 (1970).

Braun, W., Peterson, N. C., Bass, A. M., and Kurylo, M. J. "A Vacuum Ultraviolet Atomic Emission Detector. Quantitative and Qualitative Chromatographic Analysis of Typical C, N, and S Containing Compounds," Journal of Chromatography 55, 237 (1971).

Milligan, D. E. and Jacox, M. E. "Matrix-Isolation Study of the Interaction of Electrons and Alkali Metal Atoms with Various Nitrogen Oxides. Infrared Spectra of the Species NO^-, NO_2^-, and $N_2O_2^-$." J. Chem. Phys., October 1971.

Okabe, H., "Fluorescence and Predissociation of SO_2." To be published in J. American Chem. Soc., Communications to the Editor.

Paule, R. C., "A Low Level Gas Pollution Standard," to be published in Environmental Science & Technology.

McNesby, J. R. "Pollution Measurements Lack Standards," Chemical and Engineering News, May 10, 1971.

McNesby, J. R. and Lichtenstein, S., "Measures for Air Quality Program at NBS: Getting Solid Readings on Air Pollution," to be published in Pollution Abstracts.

Freeman, D. H., Annual Progress Report (NBS Technical Note 589) describing the NBS developed liquid chromatographic apparatus.

Freeman, D. H., "Interactive Gel Networks. I. Treatment of Simple Complexation and Masking Phenomena," Analytical Chemistry, December 1971 issue.

Freeman, D. H. and Enagonio, D. P., "Interactive Gel Networks for Organic Separations," Nature, Physical Science, 230, 135 (1971).

8 issues of the MAQROSCOPE, The Measures for Air Quality Newsletter.

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